

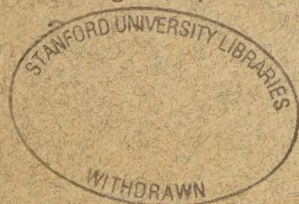
The Oxidation of d-Glucose in Sodium
Carbonate Solution in the
Presence of Copper

BY FREDERICK WILHELM JENSEN

A THESIS

PRESENTED TO THE FACULTY OF
THE GRADUATE COLLEGE OF THE UNIVERSITY OF NEBRASKA
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
DEPARTMENT OF CHEMISTRY

Lincoln, Nebraska
August 21, 1925



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INTRODUCTION

This work was undertaken with the object in view of isolating as completely as possible the oxidation products of d-glucose, when oxidized by copper in sodium carbonate solution. The oxidizing solution is a modification of Soldaini's Reagent.¹ This type of solution was chosen because its alkalinity is less than that of any other such solution hitherto studied.

Anderson,² working with Nef, studied the oxidation of d-galactose in Fehling's solution. The oxidation of d-glucose, and other hexoses, by hydrogen peroxide and air has also been studied by various investigators.

The products usually obtained in such alkaline oxidations seem to vary quantitatively rather than qualitatively. In copper oxidations, the products obtained are monobasic hexonic, pentonic, trioxybutyric, glycerinic, glycollic, and formic acids. Oxalic acid and carbon dioxide are also formed in small amounts. Oxidation by hydrogen peroxide or air give much the same products except that the hexonic acids apparently are absent.

THEORETICAL

In order to satisfactorily explain the presence of such large number of oxidation products it is necessary to consider the Lobry de Bruyn and van Ekenstein³ equilibrium.

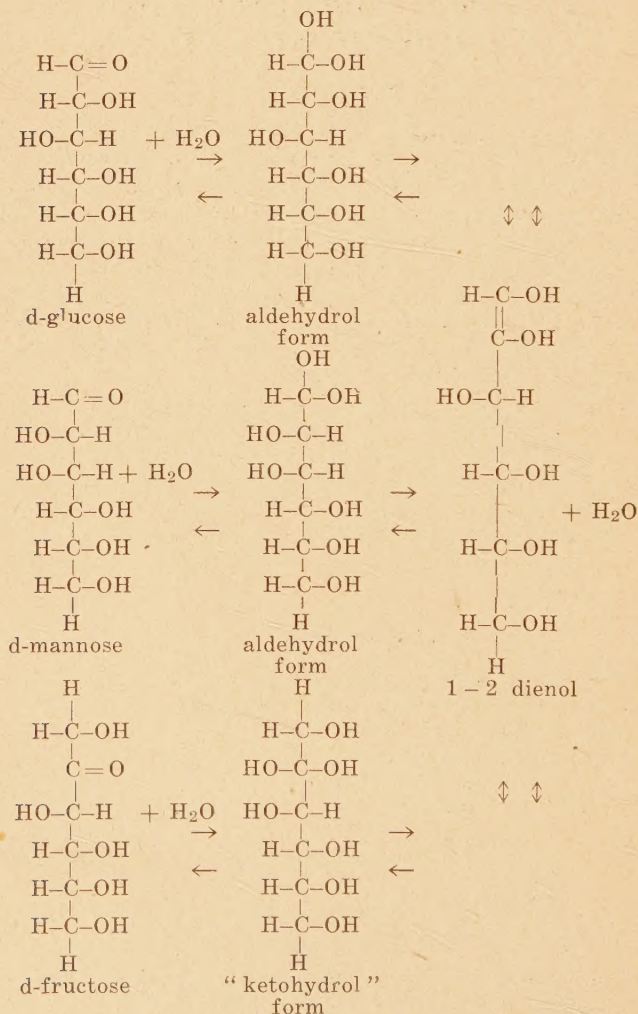
When d-glucose is placed in an alkaline solution it may add water to give the so-called aldehydrol form, and then lose it again in the same manner to give the original substance, or in a different manner so as to give a "dienol" which apparently seems to be somewhat stable in alkaline solution. This dienol, called the 1-2 dienol, may itself in turn add water in such a manner as to give either the aldehydrol form of d-glucose or the aldehydrol form of d-mannose or the "ketohydrol" form of d-fructose. Loss of water then gives the three sugars themselves. That these three are actually present has been proven by Lobry de Bruyn and van Eken-

¹ Ber., 9, 1126.

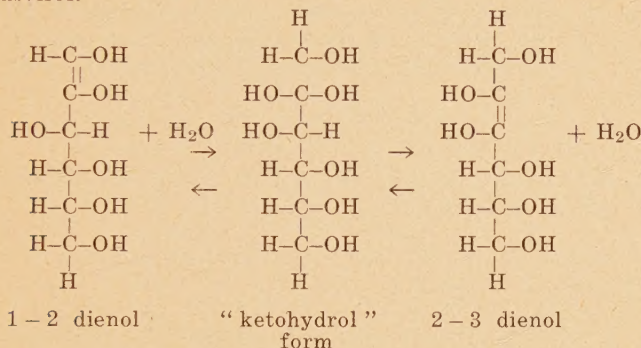
² Amer. Chem. Jour., 42, 401-431.

³ Rev. Trav. Chim., 14, 158; 15, 92; 16, 257; 19, 1.

stein, when they isolated them from the equilibrium mixture. Therefore, since these three sugars have a common dieneol, they would be expected to yield the same oxidation products. This is actually the case. The equilibrium between these three sugars is shown graphically below.



Furthermore, the "ketohydrol" form shown in equilibrium with d-fructose may lose water in such a fashion as to form a 2-3 dienol.



In the same manner as shown above, this 2-3 dienol can give rise to several new ketoses or to a 3-4 dienol. Of all the compounds present in this complex equilibrium, the dienols are by far the most reactive, and consequently are the ones to be chiefly considered in the oxidation.

Oxidation of the dienol takes place at the double bond.

According to Nef's views as explained by Glattfeld⁴ in the oxidation of d-glucose by alkaline hydrogen peroxide, the

double bond breaks, giving hydroxymethylene, $\text{HO}-\overset{\text{H}}{\underset{|}{\text{C}}}=\text{}$, and

the methylenenol of d-arabinose, $\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ | \quad | \quad | \\ \text{O} \quad \text{H} \quad \text{O} \quad \text{O} \quad \text{H} \\ | \quad | \quad | \quad | \quad | \\ =\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} \end{array}$. These

then take up oxygen to give formic acid and d-arabonic acid. Glattfeld also states that some d-ribonic acid may be formed at the same time, although he failed to isolate it. On account

of the configuration of d-ribonic acid, $\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ | \quad | \quad | \quad | \\ \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{H} \\ | \quad | \quad | \quad | \quad | \\ \text{O}=\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} \end{array}$,

of the configuration of d-ribonic acid, $\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ | \quad | \quad | \quad | \\ \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{H} \\ | \quad | \quad | \quad | \quad | \\ \text{O}=\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} \end{array}$,

⁴ Amer. Chem. Jour., 50, 133-141.

it would seem more logical to assume oxidation of at least part of the methylenol of d-arabinose to d-arabinose itself. Then, d-ribonic acid could be formed from d-arabinose by enolization and oxidation, in the same way that both d-gluconic and d-mannonic acids are formed from d-glucose.

The 2-3 dienol breaks to form a molecule of each of the



methylenols of diose, $\text{H}-\text{C}-\text{C}=\text{}$, and of d-erythrose,

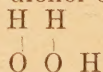


$= \text{C}-\text{C}-\text{C}-\text{C}-\text{OH}$, which take up oxygen to form glycollic,



and d-erythronic acids. d-Threonic acid, which is found to be present in slight amounts, could be explained as being formed from d-erythrose in the same manner that d-ribonic acid is formed from d-arabinose.

Similarly, the 3-4 dienol of d-glucose splits to form d and



l-glycerinic acids, $\text{O}=\text{C}-\text{C}-\text{C}-\text{OH}$, and $\text{O}=\text{C}-\text{C}-\text{C}-\text{OH}$.



The presence of d-mannonic acid as an oxidation product of d-glucose is quite readily explained, since d-mannose itself is actually present in the alkaline solutions. Both d-gluconic and d-mannonic acids evidently are the result of direct oxidation of the aldehyde sugars.

Therefore, if the above theories and assumptions are correct, the oxidation products of d-glucose, or any aldose for that matter, will consist of monobasic acids containing from one to six carbon atoms. The configuration of these acids will be the same as that of the corresponding part of the glucose chain together with the epimerides.

EXPERIMENTAL

Two hundred grams of d-glucose were oxidized in eight portions of 25 grams each. For each 25 gram portion, 275

grams of copper chloride and 275 grams of anhydrous sodium carbonate were used. This quantity of sodium carbonate was 58.3 grams in excess of the amount which is equivalent to 275 grams of copper chloride. The weight of copper chloride used was chosen somewhat in excess of the quantity necessary just for the oxidation itself,—this being roughly ascertained by previous experiment. The copper chloride and sodium carbonate, in water solution, were added together. After the addition of the glucose, also in water solution, the volume was made up to 2500 cc. The mixture was placed in a boiling water bath, and kept constantly stirred by motor. The red color of the cuprous oxide became apparent after the lapse of about one-half hour. Oxidation was complete in seven to eight hours. This is much slower than the rate in Fehling's solution as observed by Anderson,⁵ who found oxidation complete in about twelve minutes.

After completion of the oxidation, the precipitated cuprous oxide was filtered off. The solution, still containing some copper, was acidified with hydrochloric acid, and the copper precipitated with hydrogen sulphide. After filtration, the clear colorless solution was immersed in a boiling water bath, and suction was applied with the purpose of removing the excess hydrogen sulphide as rapidly as possible. Thereafter, the distillation was carried on at about 50° to 70°. The residual salt was exhausted of volatile acids as completely as possible by sweeping over with successive portions of water of 100 cc. each.

Formic Acid

Formic acid was determined by titration of an aliquot with standard alkali, and then with standard silver nitrate solution, the difference being formic acid. The amount of formic acid in a 25 gram portion varied from 3.21 grams to 3.56 grams, with the amount of formic for the 200 grams of glucose equal to 27.04 grams. A further extraction of the salt residue with concentrated hydrochloric acid and subsequent distillation, as explained below, yielded 3.82 grams more of formic acid. This made the total amount of formic acid obtained equal to 30.86 grams.

The Non-Volatile Acid Gums

The salt residue obtained was repeatedly and thoroughly extracted with 95% alcohol, yielding only 100.75 grams of

⁵ Anderson, Amer. Chem. Jour., 42, 407.

non-volatile gums. On the supposition that some of the acids might have been retained in the residue as the difficultly soluble sodium salts, the residue was extracted thrice with concentrated hydrochloric acid. In the process a crop of beautiful glycollic acid crystals separated out,—some being a centimeter and a half in length. It was possible to pick out mechanically 9.4 grams of such crystals. After recrystallization from alcohol, .1780 grams of the crystals, melting at 78°, required 23.65 cc. of .1 N alkali, thus proving their identity with glycollic acid. The dry salt residue yielded 15.3 additional grams of gum, while the distillate contained 3.82 grams of formic acid, as noted above. Thus the total yield of non-volatile gums was 116.05 grams, plus 9.4 grams of glycollic acid.

The 116.05 grams of gum were resolved into three fractions,—Fraction I, insoluble in ethyl acetate, containing hexonic acids,—Fraction II, soluble in ethyl acetate but insoluble in ether, containing pentonic, trioxybutyric, and glycerinic acids,—and Fraction III, soluble in both ethyl acetate and ether, containing glycollic and some glycerinic acids. No effort was made to determine the amount of carbon dioxide.

Fraction I, weighing 14.0 grams, was dissolved in hot alcohol, which removed 4.9 grams of salt, leaving 9.1 grams in this fraction, and reducing the weight of the gums to 111.15 grams. This fraction when treated with phenylhydrazine gave 3.41 grams of phenylhydrazides insoluble in alcohol. These phenylhydrazides were filtered, and washed with absolute alcohol. The alcohol soluble phenylhydrazides were evaporated to dryness and hydrolyzed in aqueous solution under toluene. The last traces of phenylhydrazine were removed with ether, and the gum obtained from the solution was added to Fraction II.

Fraction II, 56.25 grams in weight, was heated in aqueous solution for one hour with brucine, the amount of brucine necessary being calculated from titration of a portion of the gum. After evaporating to dryness and dissolving in the least possible amount of hot 95% alcohol, several fractions of brucine salts were crystallized out. Crop A consisted of 29.3 grams melting at 112° to 113°. Crop B was obtained in four different crops, weighing 63.5 grams, and having melting points varying from 195° to 215°. Crop C consisted of 72.4 grams of gummy brucine salts which could not be crystallized in any way. The treatment of these various crops will be discussed below.

Fraction III, weighing 33.87 grams, was heated in aqueous solution with an excess of strychnine for ten hours. After

filtration, evaporation, etc., two crops of crystalline salts were obtained. Crop A weighed 34.2 grams, and melted at 160° to 165°. Crop B weighed 25.7 grams, and melted between 200° and 230°. In addition, 22.9 grams of gummy non-crystallizable strychnine salts, called Crop C were obtained.

Glycollic Acid

Crop A, from Fraction III, was used for the identification of glycollic acid. Since Anderson⁶ gives the melting point of strychnine glycollate as 160° to 200°, this crop, melting at 160° to 165°, was considered to be nearly pure strychnine glycollate. It was converted to the calcium salt by heating in water solution with an excess of freshly slaked lime. After filtration and concentration, the salt was precipitated by adding alcohol to the hot solution and cooling. In all, 10.1 grams of calcium glycollate were obtained, corresponding to 5.9 grams of anhydrous glycollic acid. On drying at 110°, 1.0041 grams of the carefully air dried salt lost .2815 gram water. The anhydrous salt, .7226 gram, gave on ignition .2135 gram CaO.

	Calculated	Found
H ₂ O	27.48 for Ca(C ₂ H ₃ O ₃) ₂ .4H ₂ O	28.04
CaO	29.47 for Ca(C ₂ H ₃ O ₃) ₂	29.55

Thus the total yield of glycollic acid was 5.9 grams plus the 9.4 grams of free glycollic acid, mentioned above, or 15.3 grams.

d-Gluconic and d-Mannonic Acids

The 3.41 grams of alcohol insoluble phenylhydrazides, obtained from Fraction I, melted at 195° to 197°. Since d-mannonic phenylhydrazide is insoluble in cold water, this phenylhydrazide was dissolved in hot water, and gave on cooling .45 gram of highly crystalline d-mannonic phenylhydrazide. After recrystallization, and drying, the crystals melted at 214° to 215°. Fischer⁷ gives the melting point as 214° to 215°. The compound is too insoluble to determine its rotation.

From this, the characteristic brucine salt was made, .25 gram of the hydrazide giving .43 gram of recrystallized brucine d-mannonate. It melted at 212°, and an optical determination gave $[\alpha]_{D^{20}} = -27.4^\circ$, i.e., .4169 gram of the

⁶ Anderson, Amer. Chem. Jour., 42, 410.

⁷ E. Fischer, Hirschberger, Ber. d.d. chem. Ges., 22, 3221.

salt in 12.8115 grams of water gave $[\alpha] = -.87^\circ$ in a decimeter tube, $d=1.008$, $p=3.152$. Nef⁸ gives for brucine d-mannate: melting point, 212° , and $[\alpha]D^{20} = -26.73^\circ$.

From the water soluble hydrazides were obtained 2.5 grams of snowy white flaky crystals of d-gluconic phenylhydrazide, melting at 200° to 201° . An optical determination gave $[\alpha]D^{20} = +12.9^\circ$; i.e., .5104 gram dissolved in 16.0048 grams water gave $[\alpha] = .04^\circ$ in diameter tube; $d=1.003$, $p=3.090$. Fischer⁹ gives: melting point, 200° , and $[\alpha]D^{20} = +12^\circ$.

From .7 gram of the phenylhydrazide .98 gram of the recrystallized brucine salt, melting at 120° to 122° , was obtained. On drying in a vacuum, .7640 gram of the salt lost .0451 gram water, or 5.90%, the melting point rising to 155° to 157° . An optical determination gave $[\alpha]D^{20} = -18.9^\circ$, i.e., .6300 gram dissolved in 15.3727 grams water gave $[\alpha] = -.75^\circ$ in a decimeter tube; $d=1.007$, and $p=3.937$. For brucine d-gluconate, Nef¹⁰ gives: For the air dried salt, a melting point of 120° to 125° , and a loss of water of 5.68%. For the anhydrous salt, a melting point of 150° to 155° and $[\alpha]D^{20} = -18.76^\circ$.

d-Arabonic Acid

Crop A brucine salt of Fraction II after recrystallization had a melting point of 166° to 168° , and optical determination gave $[\alpha]D^{20} = -26.6^\circ$; i.e., .9582 gram in 22.0677 grams of water gave $[\alpha]D^{20} = -1.12^\circ$; $d=1.010$, $p=4.161$. Glattfeld¹¹ describes brucine d-arabonate as having a melting point of 167° to 170° and $[\alpha]D^{20} = -26.33^\circ$. The salt thus obtained was therefore evidently brucine d-arabonate. From 13.2 grams of the brucine salt, 3.5 grams of arabonic lactone gum were obtained.

To prove that a C_5 lactone was present, .4781 gram of gum was titrated, and was found to require 25.95 cc. of .1267 N sodium hydroxide for neutralization. The theoretical quantity for $C_5H_8O_5$ was 25.50 cc. The same weight of $C_6H_{10}O_6$ would have required 21.20 cc. of alkali, while the same weight of $C_7H_{12}O_7$ would have taken 31.98 cc. of alkali. This proves that a C_5 lactone was at hand.

In order to obtain the pure γ -lactone, the method of Glattfeld¹² was followed. By this means, .93 gram of the γ -d-arabonic lactone in fine transparent crystals was obtained from 2.2 grams of gum. These melted at 96° and gave $[\alpha]D^{20}$ of

⁸ Nef, Ann. Chem. (Liebig), 403, 306.

⁹ E. Fischer, Passmore, Ber. d.d. chem. Ges., 22, 273.

¹⁰ Nef, Ann. Chem. (Liebig), 403, 305.

¹¹ Glattfeld, Amer. Chem. Jour., 50, 147.

+73.31°, i.e., .5032 gram of the lactone dissolved in 8.6540 grams of water gave $[\alpha] = +2.05^\circ$ in a .5 decimeter tube; $d=1.022$, $p=5.495$. Ruff¹⁸ describes this lactone as melting at 97° to 98° and having $[\alpha]_{D^{20}} = +73.73^\circ$.

The lactone crystals were also titrated with standard alkali; .3822 gram lactone required 20.50 cc. of .1267 N sodium hydroxide, whereas the theoretical amount was 20.38 cc.

From .65 gram of the gum, .85 gram of the phenylhydrazide was obtained, the purified crystals melting at 213° and giving $[\alpha]_{D^{20}} = -13.8^\circ$, i.e., .7552 gram in 16.5461 grams of water gave $[\alpha]_{D^{20}} = -61^\circ$ in a decimeter tube; $d=1.011$, $p=4.365$.

Ruff¹⁴ and Glattfeld¹⁵ give as the melting point of d-arabonic phenylhydrazide, 214°, and 213° to 214°, respectively. Spoehr¹⁶ gives $[\alpha]_{D^{20}} = -13.9^\circ$. These constants prove that d-arabonic acid was present in the oxidation mixture.

d-Erythronic Acid

Recrystallization of Crop B of Fraction II, i.e., the high-melting brucine salts gave a crop of hard shiny crystals melting at 212° to 213°, and weighing 16.4 grams. An optical determination gave $[\alpha]_{D^{20}} = -24.4^\circ$, i.e., .6409 gram dissolved in 13.7291 grams of water gave $[\alpha] = -1.10^\circ$; $d=1.012$, $p=4.460$. The constants of this salt indicated that it was brucine d-erythronate, since Ruff¹⁴ gives: melting point, 212° to 214°, and $[\alpha]_{D^{20}} = -23.5^\circ$, while Glattfeld gives $[\alpha]_{D^{20}} = -25.6^\circ$.

The free lactone was obtained in beautiful radiating crystals, which after extraction with a hot mixture of ethyl acetate and ether, melted at 102°, and gave $[\alpha]_{D^{20}} = -72.8^\circ$, i.e., .1457 gram in 13.6670 grams of water gave $[\alpha] = -.77^\circ$ in a decimeter tube; $d=1.002$, $p=1.055$. Ruff¹⁸ gives the melting point of d-erythronic lactone as 102° to 103°, and its specific rotation as -73.3° .

In order to determine definitely that a C₄ lactone was present, a titration was performed. In order to neutralize .0849 gram of lactone 26.83 cc. of .0272 N sodium hydroxide were required, whereas the theoretical is 26.45 cc. These facts proved conclusively that the lactone isolated was d-erythronic lactone.

¹² Glattfeld, Amer. Chem. Jour., 50, 142.

¹³ Ruff, Ber. d.d. chem. Ges., 32, 507.

¹⁴ Ruff, Ber. d.d. chem. Ges., 32, 557.

¹⁵ Glattfeld, Amer. Chem. Jour., 50, 144.

¹⁶ Spoehr, Amer. Chem. Jour., 43, 240.

¹⁷ Ruff, Ber. d.d. chem. Ges., 32, 3679-80.

¹⁸ Ruff, Ber. d.d. chem. Ges., 32, 3679-80.

d-l-Glycerinic Acid

The brucine salts from the brucine d-erythronate were evaporated to dryness, dissolved in water, decomposed with sodium hydroxide, etc., and united with the gums from Crop B, Fraction III. An attempt to make a separation of d and l-glycerinic acids, according to the method of Anderson¹⁹ by the use of the quinine salts, was unsuccessful. Consequently the brucine salts were reformed, since brucine d-l-glycerinate is slowly resolved into its components by extraction with alcohol.

The constants for the brucine d-l-glycerinate, 29.3 grams, thus obtained, were: melting point, 198° to 200°, and $[\alpha]_{D^{20}} = -29.3^\circ$; i.e., .4471 gram dissolved in 15.2644 grams water gave $[\alpha] = -.84^\circ$; $d=1.008$, $p=2.845$.

Since brucine d-glycerinate is less soluble in alcohol than its antipode, the salt was extracted with hot absolute alcohol. The 20.2 grams, thus obtained, melted at 210° to 212°, and gave $[\alpha]_{D^{20}} = -30.6^\circ$; i.e., .3732 gram in 14.9904 grams water gave $[\alpha] = -.75^\circ$ in a decimeter tube; $d=1.008$, $p=2.429$. These crystals were dissolved in 90% alcohol, recrystallized, and extracted again,—this process being repeated four times. After the fourth time, the 9 grams of crystals obtained melted at 218° to 219°, and gave $[\alpha]_{D^{20}} = -31.5^\circ$; i.e., .7493 gram in 17.8801 grams of water gave $[\alpha] = -1.28^\circ$ in a decimeter tube, $d=1.011$, $p=4.022$. These constants prove that it was nearly pure brucine d-glycerinate although still containing some racemate, since Anderson²⁰ gives for brucine d-glycerinate: melting point, 222°, and $[\alpha]_{D^{20}} = -33.2^\circ$. From this, 1.55 grams of the free acid were obtained, .0776 gram of which required 26.20 cc. of .0272 N alkali, whereas the theoretical amount is 26.91 cc. No rotation was attempted, because of the low rotation, Frankland and Frew²¹ giving $[\alpha]_{D^{20}} = +2.14^\circ$.

The calcium salt was made in the usual fashion, and gave: melting point, 137°, and $[\alpha]_{D^{20}} = -8.8^\circ$; i.e., .6548 gram in 15.1398 grams of water gave $[\alpha] = -.37^\circ$ in a decimeter tube; $d=1.011$, $p=4.146$. Since Anderson²² gives for calcium d-glycerinate: melting point, 137°, and $[\alpha]_{D^{20}} = -10.2$, these determinations show that d-glycerinic acid has been isolated, although mixed with a little of the racemate.

¹⁹ Anderson, Amer. Chem. Jour., 42, 423.

²⁰ Anderson, Amer. Chem. Jour., 42, 423.

²¹ Frankland, Frew. Jour. Chem. Soc., 60, 97.

Analysis of the salt gave:

	Weight of sample	Loss on drying at 105 to 110	% (Calc.)	% (Found)
1.	.3604	.0472	12.59	13.10
2.	.3293	.0534	12.59	16.23

The percentages are calculated for $\text{Ca}(\text{C}_3\text{H}_5\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$.

Ignition gave the following values:

	Weight of sample	Weight of CaO	% CaO (Calc.)	% CaO (Found)
1.	.3132	.0687	22.40	21.94
2.	.2758	.0630	22.40	22.83

The percentages are calculated for $\text{Ca}(\text{C}_3\text{H}_5\text{O}_4)_2$.

Brucine l-glycerinate was obtained by crystallization and extraction with alcohol, the extract being saved each time for the next operation. After five such extractions, 3.8 grams of brucine salt were obtained having a melting point of 218° to 219° , and $[\alpha]_D^{25} = -23.0^\circ$; i.e., .4992 gram in 12.8505 grams of water gave $[\alpha] = -.87^\circ$ in a decimeter tube, $d = 1.010$, $p = 3.739$. Anderson gives for this salt: melting point, 222° , and $[\alpha]_D^{25} = -22.02^\circ$. From this, .46 gram of the calcium salt was obtained, melting at 134° . On drying at 105° , .4336 gram lost .0525 gram of water, or 12.1%, whereas the theoretical amount is 12.59%. The .3811 gram of anhydrous salt in 8.4792 grams of water gave $[\alpha] = +.29^\circ$ in a .5 decimeter tube, $d = 1.012$, $p = 4.301$, or $[\alpha]_D^{20} = +13.3^\circ$. Anderson gives $[\alpha]_D^{25} = +15.53^\circ$. The calcium in the solution was precipitated as the oxalate, and ignited, giving .0829 gram CaO or 21.74%. The theoretical amount is 22.40%.

In this way, it was possible to demonstrate the presence of both the d and l forms of glycerinic acid in the oxidation mixture.

d-Threonic Acid

The brucine salts in the filtrate from the brucine d-l-glycerinate gave .07 gram of phenylhydrazide, having a melting point of 156° to 160° , $[\alpha]_D^{25} = -23^\circ$; i.e., .0672 gram in 13.7568 grams of water gave $[\alpha] = -.11^\circ$; $d = 1.000$, $p = .486$. The melting point of d-threonic phenylhydrazide, according to Anderson,²² is 158° and its specific rotation is -31.17° . The melting point of the d-erythronic phenylhydrazide according to Ruff,²³ is 128° , and its specific rotation is $+17.5^\circ$. This would seem to indicate the presence of d-threonic acid, although it was impossible to get enough to definitely establish its presence.

²² Anderson, Amer. Chem. Jour., 42, 423.

²³ Anderson, Amer. Chem. Jour., 42, 423.

²⁴ Ruff, Ber. d.d. chem. Ges., 32, 3680.

d-Ribonic Acid

An attempt to make the cadmium salts from Crops C of Fractions II and III, gave no evidence of the presence of cadmium d-ribonate.²⁵ Formation of the phenylhydrazide gave only a trace of an insoluble phenylhydrazide, apparently d-gluconic phenylhydrazide.

CONCLUSION

Oxidation of d-glucose by copper in sodium carbonate solution was found to give the same general products as other copper oxidations. The relative amounts of the individual products vary, the tendency being to form much less of the hexonic acids. For example, with Fehling's solution, Anderson isolated 18 grams of hexonic acids from 118 grams of d-galactose, whereas in this case only 1 to 2 grams of hexonic acids were isolated from 200 grams of d-glucose.

The products from 200 grams of d-glucose totalled 142 grams of which the following amounts of the individual acids were isolated:

30.86 grams of formic acid.

15.3 grams of glycollic acid, identified as the free acid and as the calcium salt.

1 - 2 grams of d-gluconic acid, identified as the phenylhydrazide, and the brucine salt.

.1 gram of d-mannonic acid, identified as the phenylhydrazide and as the brucine salt.

29 grams of brucine d-arabonate, equivalent to about 6 grams of the free acid, identified as the lactone.

16.4 grams of brucine d-erythronate, identified as the lactone.

30 grams or more of brucine d-l-glycerinate, from which it was possible to isolate 9 grams of nearly pure brucine d-glycerinate and 3.8 grams of nearly pure brucine l-glycerinate.

d-Threonic acid was also probably present in very slight amounts.

One or two facts might be pointed out as important. Since Anderson obtained a relatively much greater amount of

²⁵ Fischer, Piloty, Ber. d.d. chem. Ges., 24, 4216.

hexonic acids, it would seem that a greater degree of alkalinity favors direct oxidation of the free aldehyde form.

At the same time, it must not be overlooked that a greater degree of alkalinity also favors enolization to a greater extent. This seems to be born out by the fact that the ratio of d-talonic acid to d-galactonic acid, as found by Anderson, is greater than the ratio of d-mannonic acid to d-gluconic acid, as found in this experiment. This may possibly also account for the fact that d-threonic acid was not found in large enough quantities for positive identification.

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